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(54) Branched and hydrogenated block copolymer and process for its preparation.

(57) A branched and hydrogenated block copolymer is described which is represented by the general formula $[-(EB)_1-HT-A-(EB)_2]_nX$, where $(EB)_1$ and $(EB)_2$ are hydrogenated polydiene blocks, A is a polyvinylaromatic block, HT is a random copolymer segment composed of hydrogenated dienic and vinylaromatic monomer units, X is a coupling radical having a valence equal to n, and n is an integer of from 3 to 20.

Said block copolymer shows excellent mechanical characteristics and resistance to atmospheric agents, even when used in combination with other resins.

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The present invention relates to branched and hydrogenated block copolymers and the process for the preparation thereof.

The anionic polymerization of dienic and vinylaromatic monomers in the presence of metal-alkyl and/or metal-aryl catalysts, resulting in so-called "living polymers", is a well-known technique and is described, e.g., by M. Schwarc in "Carbanions, Living Polymers and El. Transfer Processes", Interscience Publishers, J. Wiley and Sons, New York, 1956.

With this living polymer technique it is possible, in particular, to prepare both linear and branched block copolymers, especially block copolymers of polybutadiene and polystyrene such as, for example, those described in US-A-3,078,254, 3,244,644, 3,265,765, 3,280,084, 3,594,452, 3,766,301 and 3,937,760.

These block copolymers are widely used, for example, in the fields of adhesives, in compositions with various plastic materials, in the shoe industry, etc.

One serious problem with these block copolymers is the difficulty of achieving a good balance of rheological characteristics, mechanical resistance and resistance to thermo-oxidation. For example, the well-known three-block copolymers of the type A-B-A (polystyrene-polybutadiene-polystyrene) normally show satisfactory mechanical characteristics but poor thermo-oxidation resistance. In addition, their rather high viscosity, both in the molten state and in solution, creates problems in the processing and transformation thereof. On the other hand, the known four-block $(AB)_2$ linear copolymers, containing similar polybutadiene blocks, generally have good rheological but poor mechanical properties. Similar considerations apply for linear multiblock $(AB)_n$ copolymers, where n is an integer of higher than 2 and can reach a value of about 10.

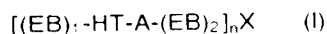
US-A-4,874,821 describes a linear copolymer with four alternating blocks, $B_1-A_1-B_2-A_2$, having defined proportions of blocks and also containing, between blocks B_1 and A_1 , a copolymeric random sequence formed by dienic and vinylaromatic monomer units. This kind of block copolymer is particularly suitable for use in adhesive formulations having good cohesion characteristics and thermo-oxidation stability.

In copending European patent application of the applicant which claims the priority of Italian patent application 21041A/90, filed on 25 July 1990, and entitled "Branched block copolymer, process for its preparation and use thereof" there is described a block copolymer of general formula $(B_1-T-A-B_2)_nX$ where B_1 and B_2 are polydienic blocks; A is a polyvinylaromatic block; T is a random copolymeric segment formed by dienic and vinylaromatic monomer units; X is a coupling radical of valence n, and n is an integer of from 3 to 20. This type of block copolymer has many potential applications and is used in accordance with its composition. In particular, copolymers with a high content of vinylaromatic monomer show excellent transparency as well as a high shock-resistance. Therefore these copolymers can be used either as such or in admixture with common thermoplastic polymers, for example polystyrene, to afford manufactured articles which can be used, e.g., in the food packaging industry. Moreover, copolymers having a low content of vinyl-aromatic monomer units and a weight ratio of blocks B_2 to blocks B_1 close to unity, can be combined with oils and asphaltic resins to give adhesive formulations with good adhesion and cohesion characteristics.

Furthermore, copolymers having an A block content of about 30 to 40% by weight and a weight ratio of blocks B_2 to blocks B_1 of about 10/1, when mixed with bitumen, afford manufactured articles showing good resistance to high and low temperatures.

It was found that by hydrogenating the diene units of the above copolymer of formula $(B_1-T-A-B_2)_nX$, it is possible to obtain a further and unexpected improvement of some characteristics thereof, particularly the mechanical properties and the resistance to thermo-oxidation and to atmospheric agents.

In accordance with the above, the present invention provides a branched and hydrogenated block copolymer of general formula (I):



wherein

$(EB)_1$ and $(EB)_2$ are hydrogenated polydiene blocks (preferably blocks derived from one or more dienes having 4 to 12 carbon atoms, such as butadiene and isoprene);

A is a polyvinylaromatic block (preferably a block derived from one or more vinylaromatic monomers having 8 to 20 (e.g. 8 to 12) carbon atoms and optionally containing halogen atoms, such as styrene, α -methylstyrene and chloro-substituted derivatives thereof);

HT is a random copolymer segment formed by hydrogenated dienic and vinylaromatic monomer units;

X is a coupling radical having a valence equal to n; and n is an integer of from 3 to 20;

the above copolymer having a weight average molecular weight of from about 60,000 to about 500,000 (preferably about 100,000 to about 350,000); an A block content of from about 20 to about 80% by weight

of the total copolymer: an $[(EB)_1 + (EB)_2]$ block content of from about 20 to about 80% by weight; a weight ratio of blocks $(EB)_1$ to blocks $(EB)_2$ of from 0.1 to 1.0; and a HT segment content of from 0 to about 40% by weight.

In the present invention, "branched and hydrogenated block copolymer" means that the degree of hydrogenation of the diene units in the copolymer is preferably at least equal to 80%, and particularly ranges from 95 to 100%.

In the present invention, preferably the weight ratio in the branched and hydrogenated block copolymer of blocks $(EB)_1$ to blocks $(EB)_2$ (which may be derived from the same or different diene(s) and are preferably formed by the same diene(s)) varies from 0.2 to 0.5, the copolymeric segment HT content ranges from 5 to 40% by weight of the block copolymer and n is an integer of from 3 to 10.

It is most preferred that in the branched and hydrogenated block copolymer (I) block A is a polystyrene block and blocks $(EB)_1$ and $(EB)_2$ are hydrogenated polybutadiene blocks, the segment HT is a random copolymer of hydrogenated butadiene units and styrene units in quantities preferably ranging from 10 to 30% by weight of the copolymer, n is 3 or 4 and X represents $=Si=$ or $CH_3Si=$.

The branched and hydrogenated block copolymer of the present invention can be used particularly in those fields of application where the maximum level of mechanical characteristics such as shock resistance as well as stability to thermooxidation and resistance to atmospheric agents is required. In particular, said copolymer is suitable for use in combination with bitumen for special applications, in adhesive formulations, in the production of manufactured articles which have to satisfy certain aesthetical requirements and in compositions with polyolefins (e.g. polyethylene, polypropylene and polystyrene) for applications in the car industry.

The present invention also comprises processes for the production of the branched and hydrogenated block copolymer of general formula (I).

More specifically, when the copolymeric sequence HT is present in the block copolymer (I), the process for its preparation comprises the following successive steps:

(a) Polymerization, by means of the living polymer technique, of a mixture of predetermined quantities of diolefin and vinylaromatic monomers until a complete, or almost complete, conversion of the monomers is achieved. Thus, a living copolymer of the type B_1-T-A is obtained.

(b) Addition of a predetermined amount of diene monomer to the copolymer obtained in step (a) and polymerization until a complete, or almost complete, conversion of the added diene monomer is achieved. Thus, a living copolymer of the type $B_1-T-A-B_2$ is obtained.

(c) Coupling of the living polymeric chains obtained in step (b) by means of a polyfunctional coupling agent. Thereby the branched block copolymer of formula $(B_1-T-A-B_2)_nX$ is obtained.

(d) Hydrogenation of the diene units of the copolymer obtained in step (c) by means of catalytic hydrogenation. The branched and hydrogenated block copolymer (I) having the copolymeric segment HT, $[(EB)_1-HT-A-(EB)_2]_nX$, is thus obtained.

(e) Recovery of the branched and hydrogenated block copolymer obtained in step (d).

Using the procedure described above, it is possible to vary the composition and length of the copolymeric segment HT by adding polar compounds, such as ethers and amines, to the reaction system.

When the copolymeric sequence HT is not present in the block copolymer of general formula (I), the process for its preparation comprises the following successive steps:

(a) Polymerization, by means of the living polymer technique, of a predetermined amount of diolefin until a complete, or almost complete, conversion of the polyolefin is achieved. Thereby a living polymer B_1 is obtained.

(b) Addition of a predetermined amount of vinylaromatic monomer to the polymer obtained in step (a) and polymerization until a complete, or almost complete, conversion of the fed vinylaromatic monomer is achieved. Thus, a living copolymer of the type B_1-A is obtained.

(c) Addition of a predetermined amount of diolefin to the copolymer obtained in step (b) and polymerization until the complete, or almost complete, conversion of the fed diolefin is achieved. Thus, a living copolymer of the type B_1-A-B_2 is obtained.

(d) Coupling of the living polymeric chains obtained in step (c) by means of a polyfunctional coupling agent. Thereby a branched block copolymer of formula $(B_1-A-B_2)_nX$, without the copolymeric segment T in its molecule, is obtained.

(e) Hydrogenation of the diene units of the copolymer obtained in step (d) by means of catalytic hydrogenation. The branched and hydrogenated block copolymer (I) without the copolymeric segment HT, $[(EB)_1-A-(EB)_2]_nX$, is thus obtained.

(f) Recovery of the branched and hydrogenated block copolymer obtained in step (e).

In particular, the polymerization steps are preferably carried out in an aliphatic and/or cycloaliphatic

organic solvent, at temperatures ranging from 30 to 150° C and at a pressure equal to or higher than atmospheric pressure, in the presence of metal-alkyl or metal-aryl catalysts. The most preferred solvents are n-hexane and cyclohexane, while the most preferred reaction temperature ranges from 50 to 100° C and the most preferred catalyst is alkyl lithium wherein the alkyl group preferably contains from 3 to 7 (e.g. 4 to 6) carbon atoms. Said catalyst generally is used in amounts of from 0.025 to 0.20 parts by weight per 100 parts by weight of the total monomers. In the polymerization mixture, polar compounds such as ethers and amines can be present, usually at a maximum concentration of about 0.1% by weight with respect to the solvent.

In the coupling step, it is preferable to work at a temperature ranging from 110 to 125° C and in the presence of a coupling agent, preferably selected from esters of (aliphatic and aromatic) dicarboxylic acids, halogen derivatives of (aliphatic and aromatic) hydrocarbons, chlorine derivatives of (aliphatic and aromatic) silanes, arenes containing unsaturated hydrocarbon radicals and the tri- and tetrachloro derivatives of silicon, tin and germanium. From a practical point of view it is most preferred to use silicon tetrachloride and/or CH_3SiCl_3 as coupling agent. The most preferred diolefin is butadiene and the most preferred vinylaromatic monomer is styrene.

In the hydrogenation step it is preferred to operate in the presence of a hydrogenation catalyst, with a hydrogen pressure of from 20 to 1,000 psi and at a temperature of from 30 to 200° C. Most preferred are a hydrogen pressure of from 150 to 600 psi and a temperature of from 40 to 130° C. Suitable catalysts are those which are well known in the art, preferably those obtained by contact of an aluminum alkyl compound with a nickel and/or cobalt compound.

At the end of the hydrogenation reaction, the branched and hydrogenated block copolymer can be recovered from the reaction mixture, after having separated the catalytic residues, by means of conventional techniques, such as by coagulation effected by treating the polymeric solution with alcohols and/or an excess of water, containing suitable reagents for the elimination of the catalytic residues.

The following examples are intended to give a more detailed illustration of the present invention without being a limitation thereof.

Example 1

1,200 g of anhydrous cyclohexane containing 2.0 g of tetrahydrofuran and 30 g of butadiene are charged into a 2 liter reactor under stirring. The temperature of the mixture is brought to 55° C and 0.220 g of sec-butyllithium in n-hexane solution are then added. After 15 minutes of reaction the temperature of the mixture reaches 70° C and the conversion of butadiene is almost complete. 150 g of styrene are then added and after 15 minutes of reaction the temperature of the mixture reaches 80° C and the conversion of styrene is almost complete. 20 g of butadiene are then added. After 10 minutes of reaction the temperature of the mixture reaches 87° C and the conversion of the added butadiene is almost complete. 0.160 g of silicon tetrachloride, dissolved in cyclohexane, are finally added and after 5 minutes the coupling reaction of the living chains is practically complete (97% yield).

A block copolymer of the type $(\text{B}_1\text{-A-B}_2)_n\text{X}$ where B_1 and B_2 are butadiene blocks, A is a styrene block, X = Si and n = 4 is thus obtained, said copolymer having the following characteristics:

- MW	250,000 (weight average molecular weight determined by GPC analysis)
- Total styrene	75 % (by weight on the total styrene, determined by IR analysis)
- Styrene in the blocks	75 % (by weight, determined by decomposition with OsO_4)

The solution of the block copolymer is transferred into a stirred 2 liter reactor, under a hydrogen atmosphere. The mass is heated to 60° C and a catalyst mixture, prepared by mixing 0.109 g of nickel acetylacetonate with 0.19 g of aluminum triethyl in 20 ml of cyclohexane, is then added.

The hydrogenation reaction is carried out at 500 psi of hydrogen over a period of 3.5 hours. After this time, the hydrogenation of the butadiene units, determined by means of iodine titration, is equal to 98.8%.

The catalyst residues are separated by extraction with diluted hydrochloric acid, followed by washing with water. Upon completion of the washing, 0.2 g of 2,6-di-tert-butyl-4-methylphenol are added to the hydrogenated copolymer in cyclohexane solution. The hydrogenated copolymer is recovered by means of coagulation with a mixture of methyl alcohol and ethanol, and is then dried in a vacuum oven at 60° C for 18 hours.

Example 2

1,200 g of anhydrous cyclohexane containing 16 g of butadiene and 92 g of styrene are charged into a 2 liter reactor under stirring. The temperature of the mixture is brought to 50°C and 0.3 g of sec-butyllithium in n-hexane solution are then added. After 30 minutes of reaction the temperature of the mixture reaches 58°C and the conversion of the monomers is almost complete. 92 g of butadiene are then added and after 10 minutes of reaction the temperature of the mixture reaches 82°C and the conversion of butadiene is almost complete. 0.15 g of CH_3SiCl_3 , dissolved in cyclohexane, are finally added and after 5 minutes the coupling reaction of the living chains is practically complete (97.5% yield).

A block copolymer of the type $(B_1-A-B_2)_nX$ where B_1 and B_2 are butadiene blocks, A is a styrene block, $X = \text{CH}_3\text{Si}$ and $n = 3$ is thus obtained, said copolymer having the following characteristics:

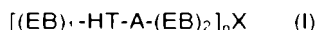
- MW	98,000
- Total styrene	46 %
- Styrene in the blocks	40 %

The solution of the block copolymer is transferred into a stirred 2 liter reactor, under a hydrogen atmosphere. The mixture is heated to 60°C and a catalyst, prepared by mixing 0.2 g of nickel 2-ethylhexanoate and 0.25 g of aluminum triisobutyl in 20 ml of cyclohexane, is then added. The hydrogenation reaction is carried out at 600 psi of hydrogen over a period of 4.0 hours. After this period of time, the hydrogenation of the butadiene units, determined by means of iodine titration, is equal to 98.5%.

The catalyst residues are separated by extraction with diluted sulphuric acid, followed by washing with water. Upon completion of the washing, 0.2 g of 2,6-di-tert-butyl-4-methylphenol were added to the hydrogenated copolymer in cyclohexane solution. The hydrogenated copolymer is recovered by means of coagulation with a mixture of methanol and ethanol, and is then dried in a vacuum oven at 60°C over a period of 18 hours.

Claims

1. Branched and hydrogenated block copolymer of general formula (I):



wherein

$(EB)_1$ and $(EB)_2$ are hydrogenated polydiene blocks;

A is a polyvinylaromatic block;

HT is a random copolymer segment composed of hydrogenated dienic and vinylaromatic monomer units;

X is a coupling radical having a valence equal to n; and

n is an integer of from 3 to 20;

the above copolymer having a weight average molecular weight of from about 60,000 to about 500,000; an A block content of from about 20 to about 80% by weight; a $[(EB)_1 + (EB)_2]$ block content of from about 20 to about 80% by weight; a weight ratio of blocks $(EB)_1$ to blocks $(EB)_2$ of from 0.1 to 1.0; and a HT segment content of from 0 to about 40% by weight.

2. Copolymer according to claim 1, wherein the degree of hydrogenation of the diene units is not less than 80% and preferably ranges from 95 to 100%.
3. Copolymer according to any one of claims 1 and 2, wherein the weight ratio of blocks $(EB)_1$ to blocks $(EB)_2$ ranges from 0.2 to 0.5; the copolymeric segment HT content ranges from 5 to 40, particularly from 10 to 30% by weight of the total block copolymer; and n is an integer of from 3 to 10, particularly 3 or 4.
4. Copolymer according to any one of claims 1 to 3, wherein block A is a polystyrene block and or blocks $(EB)_1$ and $(EB)_2$ are hydrogenated polybutadiene blocks and or segment HT is a random copolymer block of hydrogenated butadiene units and styrene units and or X is $=\text{Si}=$ or $\text{CH}_3\text{Si}=$.
5. Process for the preparation of the copolymer according to any one of claims 1 to 4, having a copolymeric block HT comprising:

- (a) polymerization, by means of the living polymer technique, of a mixture of diolefin and vinylaromatic monomer up to the complete, or almost complete, conversion of the monomers;
 (b) addition of diene monomer to the copolymer obtained in step (a) and continuation of the polymerization up to the complete, or almost complete, conversion of the added diene monomer;
 and
 (c) coupling of the living polymeric chains obtained in step (b) by means of a polyfunctional coupling agent; and
 (d) hydrogenation of the diene units of the copolymer obtained in step (c) by means of catalytic hydrogenation.

6. Process for the preparation of the copolymer according to any one of claims 1 to 4, without copolymeric block HT, comprising:
 (a) polymerization, by means of the living polymer technique, of diolefin up to the complete, or almost complete, conversion thereof;
 (b) addition of vinylaromatic monomer to the polymer obtained in step (a) and continuation of the polymerization up to the complete, or almost complete, conversion of said vinylaromatic monomer;
 (c) addition of diolefin to the product of step (b) and continuation of the polymerization up to the complete, or almost complete, conversion of said added diolefin; and
 (d) coupling of the living polymeric chains obtained in step (c) by means of a polyfunctional coupling agent; and
 (e) hydrogenation of the diene units of the copolymer obtained in step (d) by means of catalytic hydrogenation.
7. Process according to any one of claims 5 and 6, wherein the polymerization steps are carried out in an aliphatic or cycloaliphatic organic solvent at a temperature of from 30 to 150 °C and atmospheric or superatmospheric pressure in the presence of metal-alkyl and/or metal-aryl catalysts.
8. Process according to claim 7, wherein the solvent is n-hexane and/or cyclohexane, the reaction temperature ranges from 50 to 100 °C, the catalyst is a C₃-C₇-alkyllithium and said catalyst is used in amounts of from 0.025 to 0.20 parts by Weight per 100 parts by weight of the total monomers.
9. Process according to any one of claims 5 to 8, wherein the coupling step is carried out at a temperature of from 110 to 125 °C in the presence of coupling agents selected from esters of aliphatic and aromatic dicarboxylic acids, halogen derivatives of aliphatic and aromatic hydrocarbons, chlorine derivatives of aliphatic and aromatic silanes, arenes containing unsaturated hydrocarbon radicals and tri- and tetra-chloro derivatives of silicon, tin and germanium, and particularly is selected from SiCl₄ and CH₃SiCl₃.
10. Process according to any one of claims 5 to 9, wherein the hydrogenation is carried out, in the presence of a hydrogenation catalyst, under a hydrogen pressure of from 20 to 1,000 psi and at a temperature of from 30 to 200 °C.
11. Process according to claim 10, wherein the hydrogenation is carried out under a hydrogen pressure of from 150 and 600 psi, at a temperature of from 40 to 130 °C and by using a catalyst obtained by contacting an aluminum alkyl compound with a nickel and/or cobalt compound.
12. Process according to any one of claims 5 to 11, wherein the diolefin is butadiene and the vinylaromatic monomer is styrene.

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W-8000 München 40(DE)(54) **Branched and hydrogenated block copolymer and process for its preparation.**

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EUROPEAN SEARCH REPORT

Application Number

EP 91 11 2445

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	GB-A-2 061 961 (ASAHI KASEI KOGYO KABUSHIKI KAISHA) * examples * * page 2, line 5 - line 13 * * page 2, line 30 - line 61 * - - - -	1-2,4, 6-12	C 08 F 297 04 C 08 F 8.04
X	US-A-3 670 054 (H.E. DE LA MARE ET AL.) * claims 1-4 * * example * * column 3, line 10 - line 47 * * column 4, line 3 - line 10 * * column 4, line 50 - column 5, line 35 * - - - -	1-2,6-8, 10-12	
Y	GB-A-2 225 330 (ENICHEM ELASTOMERI SPA) * The whole document * - - - -	1-12	
Y	WORLD PATENTS INDEX LATEST Derwent Publications Ltd., London, GB; AN 87-139969 & JP-A-62 079 211 (ASAHI CHEMICAL IND) 11 April 1987 * abstract * - - - -	1-12	
D,A	US-A-4 874 821 (E. AGOSTINIS ET AL.) * The whole document * - - - -	1-9,12	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
A	US-A-4 291 139 (A.F. HALASA ET AL.) * claims 1-11 * * examples * * column 3, line 15 - line 49 * - - - - -	1	C 08 F C 08 G C 09 J C 08 L
The present search report has been drawn up for all claims			
Place of search		Date of completion of search	Examiner
The Hague		20 February 92	PERSSON E.K.C.
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